HOT-WATER EXTRACTION OF GROUND SPRUCE WOOD OF DIFFERENT PARTICLE SIZE

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Hot-water extraction of hemicelluloses, especially galactoglucomannans, from fractions of ground spruce wood with different particle sizes was studied at 170°C with extraction times up to 60 min. Extraction of spruce sapwood, heartwood, and thermomechanical pulp (TMP) was also compared at 160 to 180°C. Static batch extractions were carried out in an accelerated solvent extractor (ASE). The extracted hemicelluloses were characterized by sugar unit analysis and determination of acetyl groups and molar masses. The particle size significantly affected the extraction of ground wood. The total extraction yield, as well as the yields of hemicelluloses and monosaccharides, was the highest from the finest ground wood fraction (< 0.1 mm). The release of acetic acid, average molar mass of extracted hemicelluloses, and end-pH of the extracts were also dependent of the particle size, although to a lower extent. Irrespectively of the ground wood particle size, the yield of hemicelluloses reached a plateau after 40 min extraction at 170°C. The results indicate that extraction of hemicelluloses is limited mainly by the diffusion in the fiber wall, and for coarse wood shives also by the mass transfer in the wood matrix. There were only small differences in the hot-water extraction yields of hemicelluloses from spruce sapwood, heartwood, and TMP, considering both poly- and monosaccharides.

Keywords: Scetyl groups; Galactoglucomannan; Heartwood; Hot-water extraction; Molar mass; Sapwood; Spruce wood; Thermomechanical pulp

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INTRODUCTION

Lignocellulosic biomass is the most abundant class of renewable materials, accounting for about 50% of all the biomass in the world (Wingren *et al.* 2003). It represents a vast resource that could be used for production of different biofuels and bio-chemicals. In recent years, lignocellulosic hemicelluloses (non-cellulosic polysaccharides) have attracted growing interest as raw materials for not only biofuels, but also for high-value-added chemicals and materials.

Galactoglucomannans (GGMs) constitute the principal hemicellulose type in softwoods, amounting to 14 to 20% of the wood (Willför *et al.* 2005). The relative amount of GGMs in wood differs not only between wood species, but also between earlywood and latewood, sapwood and heartwood, and normal and compression wood (Bertaud and Holmbom 2004; Fengel and Wegener 1984; Timell 1967 and 1986; Willför *et al.* 2005). GGMs are found primarily in the secondary cell wall layers of softwood fibres (Meier 1985). GGMs have been reported to have an approximate degree of polymerisation of 100 to 150 (Timell 1967), corresponding to a molar mass of 16 to 24

kDa. The backbone of GGM consists of β-(1→4)-D-Man$p$ and β-(1→4)-D-Glc$p$ units at a ratio of 10:1.9 to 2.6 with side units of α-(1→6)-D-Gal$p$. The mannopyranosyl units are acetylated at C-2 and C-3 with a degree of acetylation of 0.28 to 0.37 for GGMs dissolved in TMP water (Hannuksela and Hervé du Penhoat 2004). The content of acetyl groups and galactose side units in GGMs affect the solubility of GGMs in water (Timell 1965). Deacetylation and cleavage of side chains decreases the solubility of GGMs. The molar mass for water-soluble spruce GGM from TMP has been reported to be 20 to 60 kDa (Willför *et al.* 2003; Hannuksela and Hervé du Penhoat 2004).

In recent years, research on GGMs and other hemicelluloses as a renewable biomass material has grown because of their potential applications in food, health, papermaking, textile, and cosmetic industries (Ebringerová *et al.* 2005; Willför *et al.* 2008; Mikkonen *et al.* 2008).

Extraction of hemicelluloses from wood has been studied by many techniques, such as steam explosion (Palm and Zacchi 2004), treatment with alkali (Al-Dajani and Tschirner 2008) or dilute acid (Söderström *et al.* 2003), and hot-water extraction (autohydrolysis) (Lai 2001). Most of the extraction studies have been dealing with hardwoods, because hardwoods are underutilized in many countries, and also because hardwoods are easier to fractionate by autohydrolysis. Some studies have also been done on pine wood (Yoon and van Heiningen 2008; Yoon *et al.* 2008).

Extraction of hemicelluloses from spruce wood has been studied with water at temperatures below 100°C (Örså *et al.* 1997), microwave heat-fractionation (Lundqvist *et al.* 2003), alkaline extraction (Capek *et al.* 2000), flow-through (dynamic) extraction (Leppänen *et al.* 2010 and 2011), and pressurised water extraction (Grénman *et al.* 2011; Leppänen *et al.* 2011; Song *et al.*, 2008, 2011a and 2011b). Pressurised water extraction has been carried out with Accelerated Solvent Extractors (ASE), an efficient batch extraction technique providing high repeatability and enabling extraction temperatures up to 200°C.

Many conditions and factors influence the extraction of hemicelluloses from wood, especially if the aim is to extract the hemicelluloses in high-molar-mass form. High-molar-mass GGMs may be used in novel industrial applications such as biopolymers (Ebringerová *et al.*, 1994, 2008), biofilms (Hartman *et al.* 2006a,b), and hydrogels (Gabrielii *et al.* 2000), and could also, after hydrolysis, serve as a source of sugars for fermentation to biofuel, such as ethanol, or chemicals such as 1,2,4-butanetriol, a less hazardous alternative to nitroglycerine (Niu *et al.* 2003). Extraction temperature, time, and pH are especially critical. In our previous work, we compared hot-water extraction of chips and ground wood (Song *et al.* 2008). It was found that ground wood gave better yield of GGMs extraction than chips, and pH is the key factor for high yield of structure-preserved GGM extraction. To evaluate how pH affects the extraction of hemicelluloses, extractions with different levels of $NaHCO_3$ addition prior to treatment at different pH-levels were carried out and it was found that an end-pH of extract solution about 4 was the best for high yield of high-molar-mass GGMs (Song *et al.* 2011a). In order to keep the pH around 4, extraction was carried out with different phthalate buffer solutions (Song *et al.* 2011b). In this way, it was possible to achieve a good yield of GGMs (8% of wood) in high-molar-mass form (average M_w about 10 kDa).

Lundqvist *et al.* (2002 and 2003) compared spruce hemicellulose extractions by impregnating chips with different solvents and different concentrations of NaOH

solution. Leppänen *et al.* (2010) extracted Norway spruce saw meal with pressurized hot water at 120 to 240°C using a flow-through system comparing different flow-rates. Pranovich *et al.* (2010) evaluated extraction with hot-water in two consecutive stages.

In the present study, the main objective was to evaluate the effect of wood particle size on hot-water extraction. The assessments were made mainly in terms of the overall yields of hemicelluloses, their average molar mass, and the hydrolysis of acetyl groups from GGMs. Extraction of GGMs in polymeric and/or oligomeric form was the main target. In addition, hot-water extraction of ground spruce sapwood and heartwood, as well as TMP, were compared.

EXPERIMENTAL

Spruce Wood Material

A healthy Norway spruce tree (*Picea abies* [L.] Karst.) felled in Houtskär, Southwest Finland in September 2006 was used for the wood particle size study (Song *et al.* 2008). For the study of sapwood and heartwood extractions, another healthy spruce tree felled in May 2008 was used. The wood logs had been stored in a freezer at -24°C.

Knot-free stem discs were sawn out. Sticks were cut out from the discs and were ground in a Wiley mill equipped with a 2-mm screen. The ground sapwood to be used for the particle size study was air-dried and further separated into four fractions with different particle size (<0.1, 0.25–0.5, 0.75–1 and 1.25–2 mm) using a kit of sieves and a Retac 3D vibrating sieve shaker (Retsch, Haan, Germany). The ground wood fractions were stored at -24°C in sealed polyethylene bags in the dark until extraction. For comparison of heartwood and sapwood, the ground wood samples were further ground with a 1-mm screen to obtain a fraction with a particle size smaller than 1 mm.

Thermomechanical Pulp (TMP) Material

Norway spruce TMP sampled after the second refiner was obtained from a Finnish pulp mill (UPM, Kaipola). The dry content of the pulp was about 45%.

Extraction with Water

Hot-water extraction of wood fractions with different particle sizes was performed with an ASE-200 apparatus (Dionex, Sunnyvale, CA, USA). Approximately 5 g (on dry basis) of ground sapwood (dry content about 90%) of each fraction was weighed and extracted at 170°C with 30 mL of distilled water for different time periods up to 60 min. The extract solution was purged from the extraction cell with nitrogen and the cell content was rinsed with ca. 20 mL of distilled water.

To compare extraction of sapwood, heartwood, and TMP, approximately 25 g ground sapwood (dry content about 70%) and heartwood (dry content about 80%), and 15 g TMP (all on dry weight basis) were extracted in 100-mL cells with 80 mL distilled water in an ASE-300 apparatus (Dionex, Sunnyvale, CA, USA). At the end of extraction, the cells were purged with nitrogen and the cell content was rinsed with 40 to 50 mL of water. The end-pH of the extracts was measured at room temperature shortly after the extraction. The obtained water extracts were stored at 4°C in the dark.

Analyses of Extract Solutions

Microscopy of ground wood particles was carried out using a Leica Wild MZ8 stereo microscope interfaced with a Canon PowerShot G7 digital camera.

Total dissolved solids (TDS) were determined gravimetrically after freeze-drying to a constant weight from 2-mL aliquots of the extract solutions.

Total hemicelluloses in the extracts were determined by GC after acid methanolysis, a procedure that cleaves amorphous non-cellulosic polysaccharides to monomeric methyl glycoside sugars (Sundberg *et al.* 1996). This determination comprises mainly sugar units from polymeric hemicelluloses and pectins, but it also includes mono- and disaccharides that are present in wood and/or are formed by hydrolysis during the extractions.

Monosaccharides were determined by GC of an aliquot of the extract solutions after freeze-drying and silylation of the dry residue (Willför *et al.* 2005).

Free acetic acid, released during ASE extraction, was analysed by HPLC (Agilent 1100 Series, Agilent Tech., Waldbronn, Germany) with a Synergi Hydro-RP 80R HPLC Column (250 mm × 4.6 mm, 4 µm, Phenomenex®, Torrance, CA, USA) and an RI detector (Shimadzu Corp., Tokyo, Japan) (Song *et al.* 2008).

Molar masses (M_w) of dissolved carbohydrates in extracts were determined by HPSEC (Agilent 1100 Series) equipped with a Multi-Angle Laser-Light-Scattering (MALLS) detector (miniDAWN, Wyatt Technology, Santa Barbara, CA, USA) and an RI detector (RID) (Shimadzu Corp., Tokyo, Japan) as described earlier (Song *et al.* 2008). A d*n*/d*c* value of 0.15 mL/g for GGM was used for the calculations of MALLS data (Michielsen 1999).

RESULTS AND DISCUSSION

Microscopy of Ground Wood fractions

Microscopy images of two ground wood fractions are shown in Fig. 1.

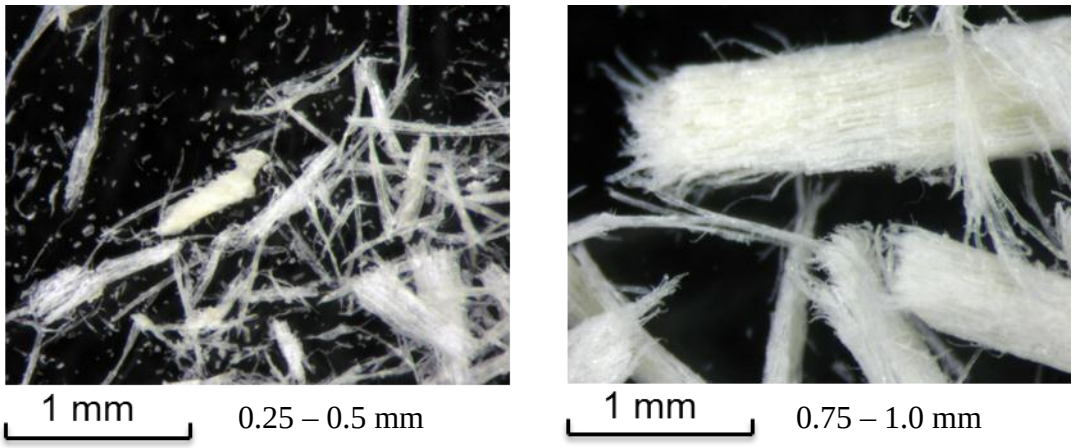

Fig. 1. Microscopy images of two ground spruce wood fractions

A large amount of fines and fibrils were seen in the 0.25 to 0.5 mm fraction. However, in the particle fraction 0.75 to 1 mm, there were only a little fines and fibrils,

and most of the fraction was made up of shives. In case of fibrils and fines, the extraction of hemicelluloses is limited mainly by the diffusion in the fiber wall. The fibers were extensively damaged and the fiber wall was opened. In the case of shives, extraction of hemicelluloses is even more difficult because of the diffusion in the wood matrix from fiber to fiber.

Extraction of Spruce Wood Fractions with Different Particle Size

The obtained extraction yield profiles are presented in Fig. 2.

Total dissolved solids of extracts

The amounts of TDS increased with the extraction time (Fig. 2a). The highest yield, about 270 mg/g (all yields here and further are given on dry wood basis), was obtained from the finest fraction (< 0.1 mm) after 50 min extraction. Coarser fractions resulted in lower TDS. The coarsest ground sapwood fraction studied (1.25 to 2 mm) gave a TDS yield that was 60 to 80% of the yield with the finest (< 0.1 mm) fraction at the same extraction time.

Total hemicelluloses in extracts

The highest yield of total poly- and oligosaccharides was obtained from the finest particle size fraction (< 0.1 mm) after a 40 min extraction, amounting to about 130 mg/g of wood (Fig. 2b). This comprises about 50% of the corresponding TDS. Coarser fractions gave lower yields of total poly- and oligosaccharides. For all fractions, the yield of total poly- and oligosaccharides leveled off after 40 min of extraction.

With an extraction time shorter than 20 min, the yields of poly- and oligosaccharides from the finest fraction were about twice the yields from the coarsest fraction. However, after longer extraction time, the differences became smaller. Acid-catalysed degradation of pentoses to furfural during extractions, especially during the extractions of finer particles, could be an explanation for this decrease, but most probably, this is because hydrolysis and cleavage of poly- and oligosaccharides to monosaccharides started to be extensive after 20 min, and was more extensive for finer fractions (Fig. 2c).

During extraction of wood with plain hot water, the glycosidic bonds in hemicelluloses are partly hydrolysed (Lai 2001; Song *et al.* 2008), and considerable amounts of monosaccharides are formed, even with the coarsest wood fraction (Fig. 2c). The amounts of monosaccharides in the extracts increased clearly along with decreasing particle size. These differences were pronounced especially after longer extraction time than 20 min. The largest amounts of monosaccharides were obtained from finest fractions, < 0.1 mm and 0.25 to 0.5 mm, after 60 min extraction, amounting in both cases to about 45 mg/g of wood. At the same extraction time, qualitative composition of extracted poly- and oligosaccharides were the same for all particle size fractions (results not shown). GGM-derived mannose, glucose, and galactose dominated in all extracts. The composition of monosaccharides was the same as well for all particle size fractions, at the same extraction time. Arabinose and xylose units had been preferentially split off, especially at early stages of extraction, but GGM-derived monosaccharides were also abundant in extracts after extended longer extraction time as shown previously (Song *et al.* 2008).

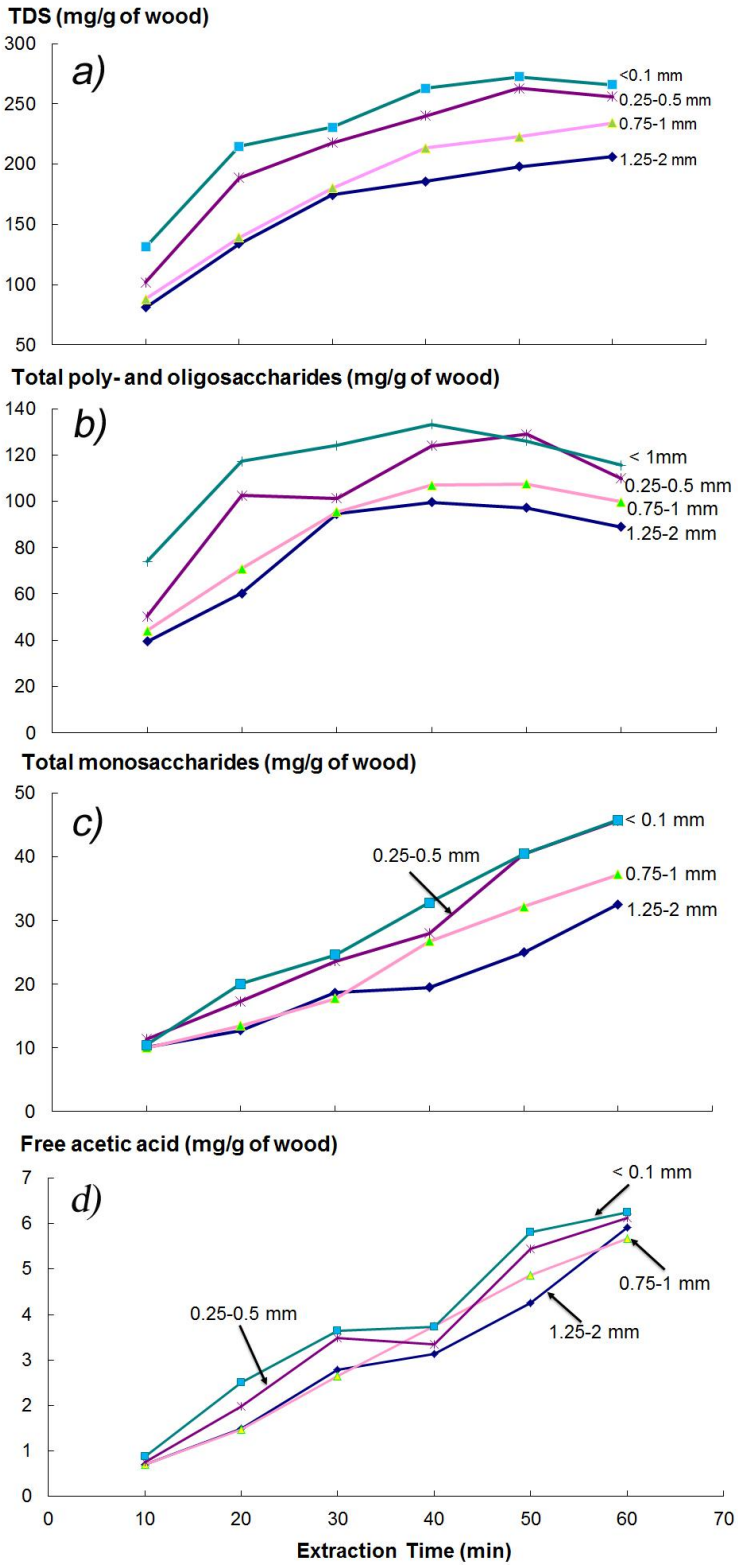

Fig. 2. Hot-water extraction yields from wood fractions of different particle size at 170°C: a) total dissolved solids, b) total amounts of poly- and oligosaccharides (calculated as anhydro-sugars based on original dry wood), c) monosaccharides, d) acetic acid released during the extraction

Hydrolysis of acetyl groups

Native GGMs in spruce wood are acetylated, carrying an acetyl group on every second mannose unit, on average and have good water solubility (Timell 1965). However, during hot-water extraction, some deacetylation of hemicelluloses will occur (Song *et al.* 2008, 2011a and 2011b), dramatically lowering their solubility (Hannuksela *et al.* 2002).

The amount of free acetic acid increased almost linearly with the extraction time (Fig. 2d). Again, the finest fraction gave the largest amounts of acetic acid, *i.e.*, the highest deacetylation of GGM during the extraction. However, the wood particle size did not have a very substantial effect on the deacetylation rate.

pH-level and average molar mass (Mw) of carbohydrates in extracts

The end-pH-level gradually decreased with the extraction time, down to a range of 3.6 to 3.7 after a 60 min extraction (Fig. 3a). The finest fraction gave the highest end-pH level. The pH-level decreased with the increase of particle size, probably, because of the higher initial pH-level of wood with finer particle size.

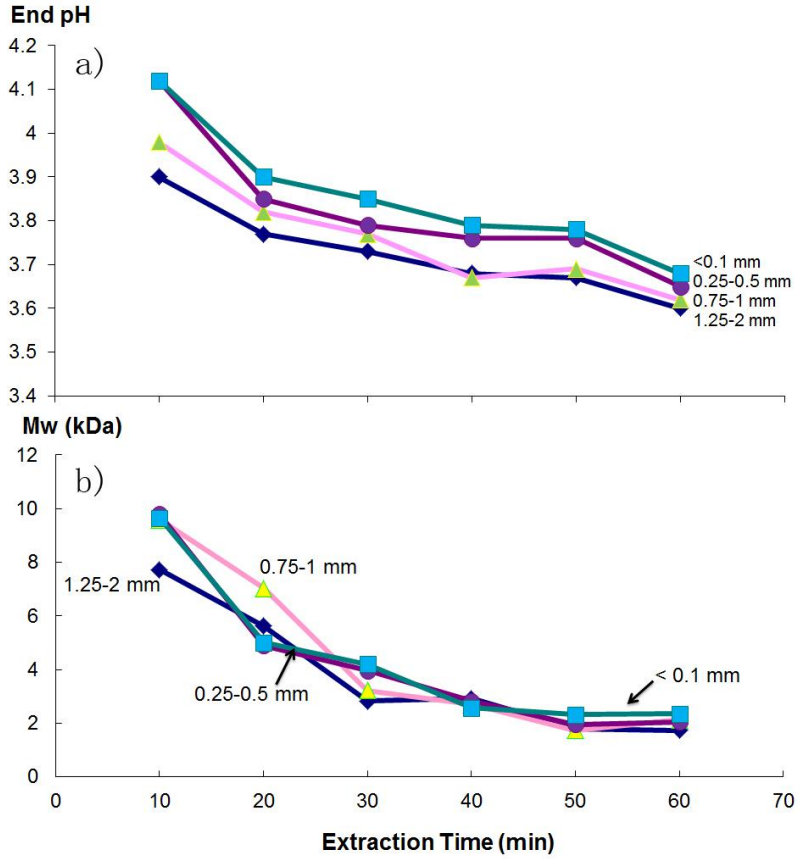

Fig. 3. a) End-pH of the water extract solutions, measured at room temperature, and b) Average Mw of extracted hemicelluloses.

High-molar-mass components were extracted at shorter extraction time (Fig. 3b). Extraction of the finest fraction for 10 min gave the highest M_w, being about 10 kDa.

However, the decrease in M_w along the extraction was almost the same and was fairly independent of the particle size.

Comparison of Spruce Sapwood, Heartwood, and TMP

The extraction profiles of sapwood, heartwood, and TMP determined at three extraction temperatures were very similar and agreed with previous results for sapwood (Song *et al.* 2008). Therefore, only extraction results at 170°C are presented and discussed here (Tables 1 and 2).

Table 1. Total Dissolved Solids (TDS), Hemicelluloses (calculated as anhydro-sugars based on original dry wood), and Free Acetic Acid in the Extract Solutions from Different Wood Materials

Yields at 170°C (mg/g of wood)	Sapwood			Heartwood			TMP		
	20 min	60 min	100 min	20 min	60 min	100 min	20 min	60 min	100 min
TDS	159	235	246	103	209	218	122	213	226
Poly- and oligosaccharides	92.7	139	119	68.5	144	130	45.1	126	108
Monosaccharides	20.7	37.3	67	10.1	29.2	46.9	10.3	30.1	52.1
Free acetic acid	3.9	7.4	11.8	2.1	7.2	12.5	1.9	5.3	9.8

At extraction times of 20 min, sapwood gave higher yields than heartwood and TMP (Table 1). However, after longer extraction time, 60 and 100 min, this difference became smaller, although the yields from sapwood were still the highest. Heartwood and TMP gave practically the same total extraction yields.

The highest yield of TDS was obtained at 170°C from sapwood after 100 min extraction. Under the same conditions, heartwood and TMP gave lower TDS yield, but slightly higher for TMP. Between 60 and 100 min extraction, the yields increased only slightly.

The different spruce wood materials gave similar yields of total poly- and oligosaccharides and monosaccharides. Sapwood gave a clearly higher yield of hemicelluloses than heartwood and TMP after 20 min extraction. This could be caused by lower end-pH level in the sapwood extract (Table 2) (Song *et al.* 2011a,b).

Heartwood and TMP exhibited similar compositions of poly- and oligosaccharides, and monosaccharides (results not shown). More glucose units were found in sapwood extracts, probably due to higher content of starch in sapwood than in heartwood, or due to lower pH of the extracts than in heartwood and TMP extracts (Table 2) (Song *et al.* 2011a,b). The sapwood also yielded more galactose units, which are probably due to the presence of compression wood.

Sapwood extraction resulted in higher amounts of free acetic acid in the extracts than with the other two materials at 170°C. However, after extended extraction time, 60 min and longer, heartwood released more acetic acid. TMP gave the lowest yield of free acetic acid, probably because part of the GGM and/or acetyl groups in GGM had already been removed with the process waters during refining in the pulp mill.

Table 2. End-pH and Average Molar Mass of the Hemicelluloses of the Extract Solutions from Three Different Wood Materials

170°C	Sapwood			Heartwood			TMP		
	20 min	60 min	100 min	20 min	60 min	100 min	20 min	60 min	100 min
pH	3.8	3.6	3.5	4.0	3.7	3.5	4.0	3.7	3.6
Average molar mass (kDa)	7.9	4.6	3.9	7.9	3.8	2.4	7.5	3.1	< 2

The amounts of released acetic acid (Table 1) correlate with end-pH of the extracts. Sapwood exhibited the lowest end-pH of the extracts (Table 2) and the highest amount of acetic acid. Slightly higher end-pH levels in extracts were obtained by TMP extraction, which is also related to the amounts of acetyl groups released.

With the same wood material, the average M_w of the extracted carbohydrates decreased with the extraction time due to hydrolytic cleavage of polymeric chains, as found before (Song *et al.* 2008). After a 20 min extraction, the average M_w of the extracted carbohydrates from the three wood materials were almost similar. However, the differences between molar-mass characteristics became substantial with the extraction time, especially after 100 min extraction.

Sapwood gave a higher average M_w of hemicelluloses in extracts than heartwood. TMP gave the lowest M_w among the three wood materials. This is, probably, because the wood material, pulp, and process waters had already been heated during the thermo-mechanical pulping process.

SUMMARY AND CONCLUDING REMARKS

1. The size of ground wood particles affected the hot-water extraction, especially during the initial stage of extraction:
    - The strongest effects were found for yields of total dissolved solids (TDS) and dissolved polymeric/oligomeric hemicelluloses.
    - Less strong effects were found for yields of monosaccharides, molar mass of dissolved carbohydrates, end-pH of extracts, and free acetic acid released during extraction.
2. After 40 min at 170°C, the degradation reactions of saccharides, including the depolymerisation, deacetylation, and degradation of monosaccharides, become dominating.
3. Extraction of hemicelluloses is limited mainly by the diffusion in the fiber wall, and for coarse wood shives also by the mass transfer in the wood matrix. Monosaccharides and acetic acid, on the other hand, will diffuse out from the fiber wall much faster than the hemicelluloses.
4. The spruce sapwood, heartwood, and TMP exhibited only small differences in extraction of hemicelluloses. Sapwood gave the highest yield of TDS, hemicelluloses, and monosaccharides, most probably due to a slightly lower pH than in heartwood and TMP.

5. When selecting the optimal particle size for industrial extraction, the energy demand in grinding of the wood also needs to be taken into account.

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